

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>B23B 1/08, 27/00, 27/08, 15/04, C08F 255/02</b>		A1	(11) International Publication Number: <b>WO 95/34396</b> (43) International Publication Date: 21 December 1995 (21.12.95)
(21) International Application Number: <b>PCT/US95/06618</b> (22) International Filing Date: 24 May 1995 (24.05.95)		(81) Designated States: AU, CA, CN, CZ, HU, JP, KR, NZ, PL, SK, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(30) Priority Data: 258,318 10 June 1994 (10.06.94) US		Published <i>With international search report.</i>	
(71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037-0001 (US).			
(72) Inventors: BALLONI, Riccardo; Via de Gasperi, 7, Vedano al-Lambro, Milano (IT). TSAI, Mingliang, Lawrence; Apartment A, 8 Pamela Lane, Rochester, NY 14618 (US).			
(74) Agents: ROBERTS, Peter, William et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037-0001 (US).			
(54) Title: FILM COMPOSITION			
(57) Abstract			
<p>A transparent multilayer film made from a polymer substrate, preferably polypropylene, is modified by a maleic anhydride modified propylene polymer, which can be located on a surface of the substrate and/or incorporated within the substrate, has a skin layer of ethylene vinyl alcohol copolymer which is coated with a transparent gas barrier layer, such as a metal oxide, specifically, silicon monoxide, silicon dioxide, aluminum oxide, magnesium oxide, boron oxide, calcium oxide and barium oxide and a mixture of two or more of the foregoing oxides.</p>			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

#### FILM COMPOSITION

The invention relates to a multi-layer film composition. More specifically, the invention relates to a transparent polymeric substrate having an ethylene vinyl alcohol copolymer 5 skin layer which is coated with a transparent barrier material.

Oriented plastic film, specifically biaxially oriented polypropylene film is widely used for packaging products, particularly foods. In its unmodified form, however, it does not have the gas and moisture barrier characteristics needed for 10 packaging.

The present invention is directed to a film composition comprising a polymeric substrate having a surface which is modified by a maleic anhydride modified propylene homopolymer or copolymer, the modified surface of the polymer substrate has 15 a skin layer of ethylene vinyl alcohol copolymer (EVOH) upon which there is a transparent gas barrier layer.

In the film of this invention, there is excellent adhesion between the polymeric substrate and the transparent gas barrier layer. The film has excellent light and microwave transparency 20 and will exhibit excellent ink adhesion without primer and excellent lamination bond strength without fracture of the barrier layer.

The invention relates to transparent multi-layer plastic films which have good gas and moisture barrier properties. 25 Typically, the transparent films permit the transmission of light waves through the film so that objects on either side of the film can be seen. The films also permit the transmission of microwaves and, therefore, they are useable in a microwave oven. Typically, the light transmission of the film is more 30 than 50%, specifically, between 70 to 90%. Light transmission is measured using a XL-211 Hazegard Hazemeter, manufactured by Pacific Scientific Co., according to the ASTM test method D1003-61.

The multilayer film structure of this invention comprises 35 a substrate of polyolefin, typically polypropylene. The preferred polypropylene matrix material has the following characteristics: density of 0.91 g/cc; melting point of 160°C

- 2 -

or higher; melt flow rate of 2 to 4.

The polyolefin substrate is modified by a maleic anhydride modified polypropylene. The maleic anhydride modified polypropylene skin layer can be prepared by any process, for 5 example, the process disclosed in U.S. 3,433,777 and 4,198,327.

A simple process for its preparation is described in U.S. 5,153,074. The maleic anhydride modified polypropylene can be interblended into the substrate, by melt blending it with the substrate polyolefin, and/or it can be coextruded with the 10 substrate polymer. A commercially available maleic anhydride modified polypropylene or propylene copolymer has the following physical characteristics: density of 0.90 (ASTM D1505), Vicat softening point of 143°C (ASTM D1525); Shore hardness of 67°C (ASTM 2240); melting point of 160°C (ASTM D2117). The maleic 15 anhydride modified polypropylene acts as a tie layer which adheres the substrate to the EVOH. It is important to use the maleic anhydride modified polypropylene since without it the substrate is incompatible with the EVOH. Maleic anhydride modified polypropylene is sold commercially by a variety of 20 sources, e.g. it is sold under the tradename "ADMER" by Mitsui, "BYNEL" by DuPont, and "PLEXAR" by Quantum.

An EVOH layer is applied to the surface of the modified substrate. Generally the ethylene content of the EVOH will not impact the properties of the film, but the gas barrier 25 properties of the film is a function of the proportion of ethylene in the EVOH. Typically, however, the ethylene content ranges from 30 to 50 mole % ethylene, but this can range from 20 to 80 mole %. The saponification number of the EVOH barrier can range from 50% or more. Conventionally, EVOH is made by 30 saponifying ethylene vinyl acetate copolymer (EVA). If the saponification is incomplete, the end product will be a blend of EVOH and EVA. Since EVA is a tacky material (low melting point) which has poor gas barrier properties, its presence in the blend will hinder the gas barrier properties of the film.

35 In instances where the substrate is coextruded with the maleic anhydride modified polypropylene, it is important to apply the EVOH to the modified surface, otherwise, the EVOH will

- 3 -

have difficulty adhering to the substrate. The EVOH can be applied in a thin layer by any effective process. The layer can range in thickness from 0.01 mil to 0.20 mil. Three processes of note are 1) coextrusion of a EVOH skin and the modified 5 substrate with the use of a selector plug or multicavity die; 2) extrusion coating the EVOH layer onto the surface of the modified substrate; 3) co-lamination of a thin film of EVOH onto the surface of the modified polypropylene sheet.

For extrusion coating and co-lamination, it is useful, but 10 not mandatory, to corona or flame treat the bonding surface of the substrate (the maleic anhydride modified polypropylene side) prior to application of the EVOH. This can minimize potential delamination problems.

A heat sealable film can be applied to the substrate on the 15 side opposite to the EVOH. This can be accomplished by coextruding a heat sealable polymer, copolymer or trimer, such as ethylene-propylene-butene, onto the substrate. The heat sealable layer employed herein and applied during coextrusion can be an ethylene propylene (EP) copolymer or an ethylene 20 propylene butene-1 (EPB) terpolymer which, as noted above is, typically, located opposite the EVOH skin layer. The ratio of ethylene to propylene to butene-1 can be from 0 to 15% ethylene, 70 to 100% propylene and 0 to 15% butene-1; that is, 2% ethylene, 94% propylene and 4% butene-1.

25 The multilayer films of this invention will generally range in thickness from 0.50 to 3.00 mil (12.5 to 75  $\mu\text{m}$ ). The thickness of the core layer is usually about 90% of the total thickness of the film, but this can range from 79 to 94% with the other layers making up the difference. For instance, the 30 heat seal layer is typically 3 to 10% of the total thickness of the film and the maleic anhydride modified polypropylene is typically 2 to 6% of the total film thickness. The EVOH layer will range from 1 to 5% of the total film thickness.

The EVOH skin is then coated with a transparent barrier 35 layer by deposition of a transparent gas barrier material thereon. Typical materials useful as a barrier layer include metal compounds or alloys. Specific examples include silicon

- 4 -

carbide, oxides, ceramics such as silicon monoxide, silicon dioxide, aluminum oxide, magnesium oxide, boron oxide, calcium oxide and barium oxide. Organic compounds such as diamond-like compounds are also contemplated. Mixtures of two or more of the 5 foregoing barrier materials can also be employed, a specific mixture which has demonstrated advantages is a mixture of the following oxides: silicon dioxide, aluminum oxide, calcium oxide, magnesium oxide, boron oxide and barium oxide. Usually a major proportion of the mixture is silicon dioxide which can 10 be more than 50% of the mixture. A number of other oxide materials can be used to make-up the remaining proportion. Usually, they are each present in amounts of less than 20% of the total amount of the mixture. A mixture of oxides have been found to provide improved barrier properties. Any typical 15 process for depositing the transparent barrier material onto the EVOH layer known in the art can be employed. The EVOH surface adheres well to the transparent barrier material.

The transparent barrier material can be deposited in numerous ways such as by physical methods, including thermal 20 heating, electron beam deposition, sputtering, electroplating or chemical methods such as end-products deposition inside a vacuum chamber by either chemical reactions or plasma polymerization.

We have found it advantageous to surface treat the EVOH 25 surface prior to depositing the transparent barrier material thereon. Suitable surface treatment is by flame or corona treatment.

If the film is to be used as a printable surface, it may be preferable to adhere a printable surface to the film. Skin 30 polymers which can enhance printability include polyolefin homopolymers or copolymers.

As demonstrated in the following examples, which were actually conducted, the EVOH in combination with the transparent gas barrier layer improve oxygen barrier properties over other 35 transparent structures. While, in these examples, polypropylene is the substrate, other polyolefin films may be used such as polyester, polyamide, polycarbonate and other polyolefins such

- 5 -

as polyethylene or polybutene.

The following Examples illustrate the invention.

Example 1

This example, for comparative purposes, omits the EVOH  
5 layer.

A three layer biaxially oriented film, having an approximate final thickness of 0.70 mil (17.0  $\mu\text{m}$ ), was prepared by coextruding a primary polypropylene layer (density 0.907, melting point 167°C, and a melt flow rate of 3) comprising 90%  
10 of the film thickness and an oxide receiving upper surface layer of a maleic anhydride modified polypropylene (density 0.907, melting point 160°C), comprising 5% of the total film thickness, and a lower surface layer of heat sealable resin comprising 5%  
15 of the total thickness of ethylene-propylene-butene-1 terpolymer. The coextrudate was quenched at between 30 to 50°C, reheated to 115-130°C and stretched in the machine direction 5 times using transport rolls operating at different speeds. After the desired machine direction orientation was obtained,  
20 the film was transversely oriented 8 times, at a temperature profile ranging from 155 to 180 °C. Subsequently, the transparent gas barrier receiving upper surface layer was corona discharge treated. The film was vacuum deposited with silicon monoxide as a transparent gas barrier layer. Table 1, below, shows the film properties prior to vacuum deposition of the  
25 silicon monoxide. Table 2, below, shows the film properties after vacuum deposition of the silicon monoxide.

Example 2

This is a comparison example of an opaque metallized film.

The opaque, metallized, four layer biaxially oriented film  
30 structure was prepared following the process of Example 1 with the exception that aluminum rather than silicon oxide was deposited onto the maleic anhydride modified polypropylene.

Example 3

This example demonstrates a process for making a  
35 transparent film in accordance with the present invention which has superior gas barrier properties.

A four layer biaxially oriented film structure was prepared

- 6 -

from the polypropylene core employed in Example 1. The same procedure as example 1 was followed except that a layer of EVOH was coextruded onto the modified polypropylene side of the substrate film. The ethylene content of the EVOH was about 48 5 mole %. The thickness of the EVOH layer was about 0.02 mil (0.50  $\mu\text{m}$ ). The resulting four layer coextrudate was quenched and biaxially oriented as in Example 1. Thereafter silicon monoxide was vacuum deposited onto the EVOH layer, in the same manner as disclosed in example 1.

10 Example 4

This example demonstrates a process for making another transparent film in accordance with the present invention which has superior gas barrier properties.

A four layer biaxially oriented film structure identical 15 to the film structure of Example 3 was made with silicon dioxide as the transparent barrier layer.

Example 5

This example demonstrates a process for making another transparent film in accordance with the present invention which 20 has superior gas barrier properties.

A four layer biaxially oriented film structure identical to the film structure of Example 3 was made except the transparent barrier material was a mixture of various metal oxides containing more than 50 % silicon dioxide, and the 25 remaining proportion being aluminum oxide, magnesium oxide, boron oxide, calcium oxide and barium oxide.

In the following tables, gas barrier properties were measured on the films produced by determining the Oxygen Transmission Rate (OTR) (cc/100 in<sup>2</sup>/24 hr) which was measured 30 at 73°F, 0% RH. The light transmission % was measured by a hazemeter (XL-211 Hazegard Hazemeter, manufactured by Pacific Scientific Co.) according to ASTM D1003-61. Several runs were conducted and the average of those runs is reported in the tables.

35 In the data of Table 2, the excellent water vapor barrier properties are demonstrated by the measured water vapor transmission rate (WVTR).

- 7 -

**TABLE 1**  
**FILM PROPERTIES PRIOR TO DEPOSIT OF TRANSPARENT BARRIER**

Example #	Light Transmission (%)	OTR
1	93	150

5

		TABLE 2 FILM PROPERTIES AFTER DEPOSITION OF TRANSPARENT BARRIER				
10	Example #	Barrier Material	Average Light Trans-mission (%)	OTR	WVTR	Microwavable
15	1 (non-EVOH)	Silicon Monoxide	85	120	0.55	Yes
2	2 (non-EVOH)	Aluminum	1	10	0.12	No
20	3 (EVOH)	Silicon Monoxide	84	0.15	0.40	Yes
4	4 (EVOH)	Silicon Dioxide	82	2.7	0.47	Yes
25	5 (EVOH)	Mixture of oxides	82	0.07	0.14	Yes

As shown in Table 1, before depositing the transparent gas barrier material, the light transmission properties of the film are rather good, but the oxygen barrier properties are poor. Thus, the film of example 1 would not be useful for most packaging purposes.

The data reported in Table 2 show that a high gas barrier transparent film was made in accordance with this invention. The EVOH-containing films having the transparent gas barrier deposited thereon have superior transparency and comparable gas barrier properties over non-EVOH-containing transparent and metallized films.

Comparing the data of Table 1 with the data of Table 2, it is apparent that the EVOH coupled with the metal oxide contributes to the excellent gas barrier properties of the film, demonstrated by the OTR. That is, in the film of example 1 which was made without EVOH, prior to deposit of silicon monoxide, the oxygen transmission rate was 150. After depositing the silicon monoxide, the oxygen transmission rate improved to a rate of 120. The films of examples 3, 4 and 5 which incorporate both the EVOH and the

- 8 -

metal oxide barrier material achieved excellent oxygen transmission rates of 0.15, 2.7 and 0.07, respectively.

- 9 -

CLAIMS

1. A transparent film composition which comprises a polymeric substrate having at least one surface which is  
5 modified by a maleic anhydride modified propylene homopolymer or copolymer, the modified surface of the polymer substrate has a gas barrier ethylene vinyl alcohol copolymer skin layer and a transparent gas barrier located on the ethylene vinyl alcohol copolymer skin layer.

10

2. A film composition according to claim 1 in which the maleic anhydride modified propylene homopolymer or copolymer is a discrete layer.

15

3. The film composition of claim 1 in which the substrate comprises an oriented homopolymer or copolymer of propylene.

4. The film composition of claim 1 in which one side  
20 of the film has a heat seal layer thereon.

5. The film composition of claim 1 in which the transparent gas barrier layer is a metal oxide selected from the group consisting of silicon monoxide, silicon dioxide,  
25 aluminum oxide, magnesium oxide, boron oxide, calcium oxide and barium oxide and a mixture of two or more of the foregoing oxides.

6. A process for making a transparent film composition  
30 comprising the steps of:

- (a) providing a polymeric substrate film;
- (b) modifying at least one surface of the polymeric substrate film with a maleic anhydride modified polypropylene homopolymer or copolymer;
- 35 (c) applying ethylene vinyl alcohol copolymer to the modified surface of the substrate; and
- (d) depositing a transparent gas barrier material onto

- 10 -

the ethylene vinyl alcohol copolymer surface formed in step (c).

7. The process of claim 8 in which the metal oxide gas barrier material is selected from the group consisting of silicon monoxide, silicon dioxide, aluminum oxide, magnesium oxide, boron oxide, calcium oxide and barium oxide and a mixture of two or more of the foregoing oxides.

10 8. The process of claim 8 in which the film of step (c) is stretched in the machine direction about 4 to about 7 times and then stretched in the transverse direction about 5 to about 12 times and then flame or corona treated.

## INTERNATIONAL SEARCH REPORT

International application No. PCT/US95/06618
---

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :B23B 1/08, 27/00, 27/08, 15/04; C08F 255/02

US CL :428/35.9, 36.6, 36.7, 446, 457, 461, 463, 515, 518, 520, 522, 910

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. :

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,153,074 (MIGLIORINI) 06 October 1992, Abstract; column 1, line 49 to column 3, line 41.	1-8
A	US, A, 4,181,689 (NAGATOSHI ET AL) 01 January 1980, see entire document.	1-8

Further documents are listed in the continuation of Box C.

See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

23 JUNE 1995

Date of mailing of the international search report

13 JUL 1995

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

STEPHEN SAND

Telephone No. (703) 308-2351